Nanopigments in Offset Printing Inks

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Abstract:

Nanopigments are a new type of pigment. They are hybrid materials consisting of organic dyes and layered silicate nanoparticles. Nanopigments are already applied to make polymeric coatings and they had shown improvement in mechanical, thermal and stability properties of the substrate and dyes (Batenburg and Fischer, 2001)

In this work, nanopigments had been synthesized to be applied in the manufacture of offset printing inks. Therefore, four different nanopigments are pursuit: cyan (C), magenta (M), yellow (Y), and black (K), in order to obtain primary colour for a four-colour-process system.

Keywords: Colorimetry, nanopigments, offset printing inks.

1. Introduction:

Nanopigments or Planocolors® are a new kind of pigment developed by researchers of TNO-TPD Eindhoven (Netherland). Nanopigments are hybrid materials obtained through the combination of organic dye molecules and layered clay nanoparticles, in a special phyllosilicate from the smectite group (figure 1). Nanopigments gather advantages of dyes and pigments, such as brilliant colours, wide colour gamut, while avoiding their drawbacks, like bleeding, low lightfastness, low stability against oxygen, temperature, UV radiation, etc. (Batenburg and Fischer, 2001)

Although nanopigments can be applied in a wide variety of substrates (Batenburg and Fischer, 2001) to make coatings or to colour materials, they have been used and studied mainly in the field of polymers. In fact, for decades, organically modified clays have been studied and used as reinforcing additives to improve mechanical and thermal properties in polymers (Mai, Yu, 2006), (Batenburg and Fischer, 2001)

However, nanopigments combine two important tasks: they improve physical-chemical properties of the polymer while giving colour (Batenburg and Fischer, 2001).

In this research collaboration between Colour and Vision Group from University of Alicante (CVG-UA) and Optics Colour Imaging Technological Institute (AIDO), nanopigments have been synthesized to be applied in the manufacture of offset printing inks. That is, CVG-UA has developed specific nanopigments and has supplied them to AIDO. Then, AIDO has been responsible for assessing their advantages and drawback as raw material for manufacturing offset printing inks.

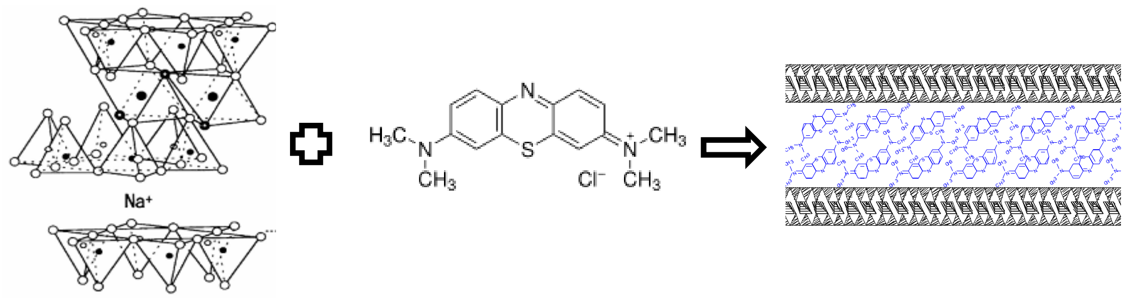

Figure 1: Schematic representation of clay sheet, dye molecule (methylene blue) and blue nanopigment.

2. Methods:

Nanopigments Synthesis:

At a laboratory scale, nanopigments are obtained in a simple process with two main steps (Batenburg and Fischer, 2001):

Firstly nanoclays have to be dispersed in a solvent, better in deionized water. This causes the nanoclay to swell. This increases the distance between clay sheets and, as a consequence, reduces the ionic bond force of the counterions of the clay.

After that, a dye solution is added to the dispersion. Then the ionic exchange takes place: Dye molecules replace counterions of the clay. This gives colour to clay nanoparticles and makes them compatible with the polymer.

At this moment, nanopigment is formed but dispersed in the deionized water. In order to isolate and purify the nanopigment we have to, firstly, wash and filter the dispersion, and then dry the cake. It can be done through several techniques: freeze drying, spray drying or in a muffle.

In figure 2 there is a schematic flowchart of laboratory synthesis process.

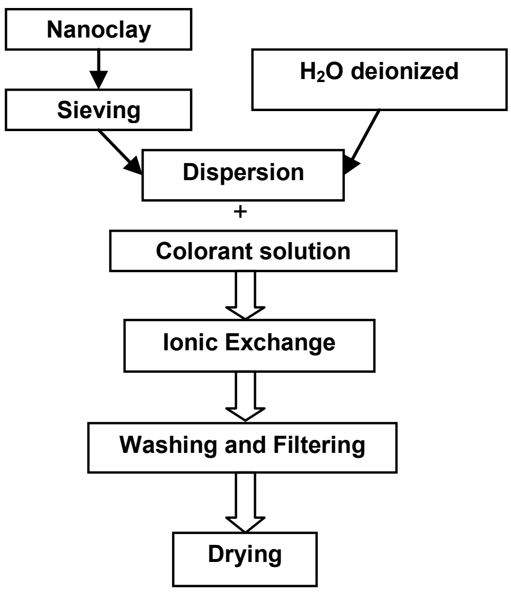

Figure 2: Scheme of nanopigments' synthesis at laboratory

As a result, a light, dry powder is obtained that can be used such as a pigment, so it can be added directly to the material to colour, or to make coatings and cover a substrate.

Nanopigments for Offset Printing Inks

The purpose of the research is to obtain primary colours for four-colour-process printing system for making offset inks. Therefore four different types of nanopigments, cyan (C), magenta (M), yellow (Y) and black (K) were obtained.

First step was selecting organic dyes. These dyes must be able to be attached to clay nanoparticles and, at the same time, match the primary colours requested (cyan, magenta, yellow or black). In table 1 there is a list of selected dyes that in advance seem to be able to reach and develop the suitable colour shade. This list is the result of a deep search in the Colour Index database (http://www.colour-index.org/).

Table 1.- Dyes selected to obtain nanopigments for primary colours in four-colour-process offset printing system.

Dye	**CIE**	**Shade**	**Supplier**
Methylene Blue	C.I. basic blue 9	Greenish blue	Sigma-Aldrich
Methyl Red	C.I. acid red 2	Red-Yellow	Sigma-Aldrich
Malaquite Green	C.I. basic green 4	Light bluish green	Sigma-Aldrich
Rodhamide 6G	C.I. basic red 1	Fluorescent bluish pink	Sigma-Aldrich
Thioflavine T	C.I. basic yellow 1	Light greenish yellow	Sigma-Aldrich
Acridine Yellow	C.I. 46025	Yellow	Sigma-Aldrich
Basic Blue 3	C.I. basic blue 3	Greenish blue	Sigma-Aldrich
Neutral Red 5	C.I. neutral red 5	Bluish red	Sigma-Aldrich
Maxilon Black		Black	Ciba
Fast Black K	C.I. Azoic disazo component 38	Black	Sigma-Aldrich

The nanoclay used to obtain nanopigmtens was montmorillonite Nanofil® 116 from Süd-Chemie. It is a phyllosilicate clay from smectite group, with a cationic exchange capacity of 120 meq/100 g_{clay}. Layers of montmorillonite particles have the shape of small flakes. The layers are 20–200 nm in diameter laterally and come in aggregates known as tactoids, which can be 1 nm or more thick (Ajayan, Schadler, Braun2003).

After synthesizing several nanopigments, which are listed in table 2, they were sent to AIDO in order to assess their suitability as raw material to make offset printing inks.

Table 2.- Nanopigments synthesized for AIDO

Nanopigment	**Dye**	**% dye**
Nnp blue 1	Methylene blue	27,5
Nnp blue 2	Basic Blue 3	30,7
Nnp magenta	Rodhamide 6G	41
Nnp yellow 1	Thioflavine T	27,2
Nnp black 1	Maxilon Black	30
Nnp black 2	Fast Black K	35,7

Nanopigment ink fabrication:

The nanopigment ink fabrication process, done in laboratory and can be explained in figure 3.

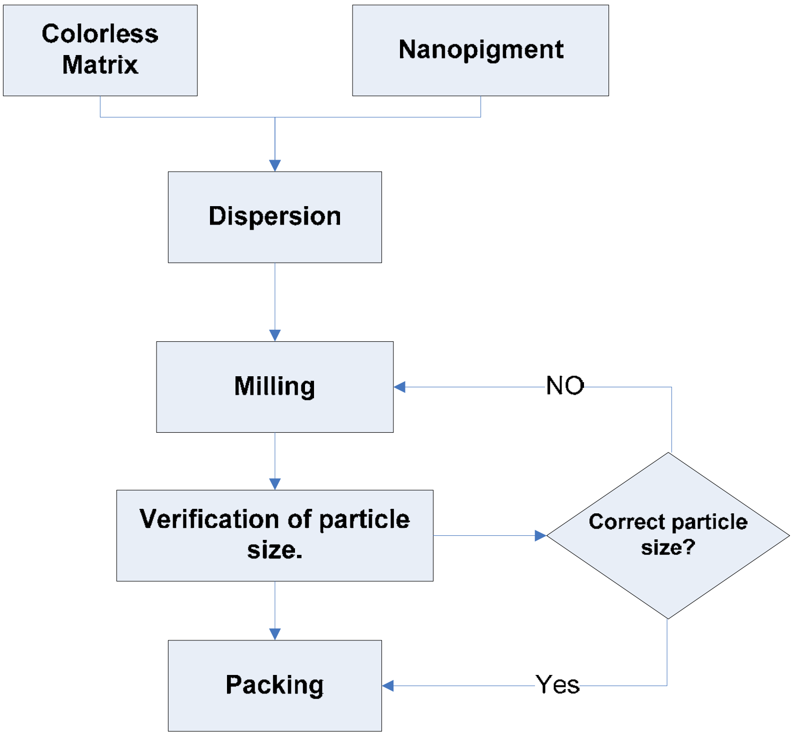

Figure 3: Nanopigment ink fabrication flowchart.

In the first place nanopigments are pre-dispersed in an uncoloured matrix, then the pigments are ground in a three cylinder mill during a period of time. After this, the particle size is checked with a Grind-o-meter. If the particle size is under 5 µ the fabrication is finished; if the particle size is over 5 µ, ink is ground again in the three cylinder mill.

Physicochemical proprieties of the obtained nanopigment inks:

Different proprieties of the nanopigmented inks obtained in laboratory have been studied to try to evaluate their behaviour as offset inks.

The more important physical proprieties for offset inks have been studied in this research.

These are:

-Particle size.

-Gloss at 60º degrees.

-Tack following the standard ISO 12634 “Determination of tack of paste inks and vehicles by a rotary tackmeter”.

-Viscosity following the standard ISO 12644:1996 “Graphic technology Determination of rheological properties of paste inks and vehicles by the falling rod viscometer.”

-Rigidity following the standard ISO 12644:1996 “Graphic technology Determination of rheological properties of paste inks and vehicles by the falling rod viscometer.”

-Grinding time, Time in minutes needed to achieve 5µ of particle size with the three cylinder mill.

- CIELab Colour, L*,a*, b* values measured by the Standard ISO 13655:1996 “Graphic technology -- Spectral measurement and colorimetric computation for graphic arts images”

- Fluidity, measured in centimetres, is the space covered by a given quantity of ink in a space of time, being more fluid the ink which covers more space.

This includes applying standard procedures (ISO, UNE, ASTM, etc.) to evaluate physical properties (rheological, etc...) chemical and optical properties (colour, etc...) of the Nanopigmented inks.

3. Results

In “*Table 3”* there is an example of the results obtained in the characterization tests of nanopigmented inks.

Table 3. Studied product: Ink made from nanopigment synthesized from "methylene blue".

Nº	Studied Property	Units	Test	Results
1	General Characteristics	n.a.		Regular dispersion, some residue after the 1st pass through three roll mill but flowing well.
2	Scope	n.a.		Offset
3	Color Index	n.a.		n.a
4	Viscosity (0'8-0.4)	Poises	ISO 12644:1996.	Starting speed= 4584, Finish speed= 599 (alter adding 13% of solvent)
5	Stiffness (0'8-0.4)	Dyna/cm^2	ISO 12644:1996.	Starting R = 20537, Finish R = 17918 (alter adding 13% of solvent)
6	Viscosity at 2.5 s-1	Pa*s	ISO 12644:1996.	n.a
7	Tack	30ºC; 100m/min.	ISO 12634 Determination of tack of paste inks and vehicles by a rotary tackmeter.	80
8	Fineness	µm	Grindometer	5
9	Milling Time	minutes	Three roll mill	35
10	Hardness		Nº of times grind is needed	2
11	CIELab Colour	n.a.	ISO 13655:1996	L = 51.4 / a = 1.9 / b = - 49.3
12	Colour strength	%	IGT tester	n.a
13	Brightness	%	Micro-gloss 60º	44
14	Fluidity	cm.	Inclined Plane 85º	27

4. Conclusions:

After preparing several nanopigment inks, some ideas can be pointed out:

-Following the bibliographic database search, we have checked that a wide number of dyes can be used to synthesize nanopigments.

-From a physical point of view, nanopigments obtained with selected dyes have a good behaviour as raw material for making offset printing ink. However, they have a major drawback; their shade is not exactly the shade requested in the standard for printing inks.

-As well as the shade difference. Due to a dye concentration between 27% and 41%, colour saturation of the inks is very small, and the high amount of nanoclays in offset inks affect to their proprieties.

-Offset inks can be prepared from the synthesised nanopigments with similar physical proprieties than the standard inks.

-Despite nanopigments having a particle size from 20 to 200 nm in diameter, due to the aggregate formation during the dispersion process, particle size in offset inks is more than 5µ. This needs to be improved in futures studies by changing the dispersion process, adding surfactant additives, or improving the drying stage.

Therefore, as future perspective, new efforts have to be done to approach nanopigments' colour shade to the standards and improve the dispersion and grinding processes. These are the main new aims for the research during the year, probably by making hybrid inks from nanopigments and standard pigments and adding surfactant additives.

Acknowledgements

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